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A LIMNOLOGICAL SURVEY OF NEARSHORE WATER OF LAKE SUPERIOR

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Environment

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A Limnological Survey of
Nearshore Water of Lake
Superior

A LIMNOLOGICAL SURVEY OF NEARSHORE
WATER OF LAKE SUPERIOR

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ABSTRACT

Up-to-date and accurate information about the existing water quality characteristics is necessary for any future planning or management of the Great Lakes environment. Four cruises on the nearshore waters of Lake Superior were carried out by the Ontario Ministry of the Environment during the late summer and fall of 1973 to provide a systematic water quality monitoring of the Ontario shoreline of the lake. This study generated extensive physical, chemical and bacteriological data on 67 stations along the north shore of the lake from Whitefish Bay to Thunder Bay. In addition to this, intensive water quality studies were undertaken in the following confined areas where industrial and municipal discharges have contributed to impairment: Peninsula Harbour, Jackfish Bay, Nipigon Bay and Thunder Bay. A comparison is made of water quality in nearshore and harbour areas including an examination of dissolved oxygen, suspended and dissolved solids, conductivity, turbidity, nitrogen, phosphorus, phenols, alkalinity, chloride, sulphate, pH, heavy metals, dissolved silica, water temperature, chlorophyll a, total and fecal coliforms and fecal streptococci.

Extensive bottom sediment studies were incorporated in the survey program to determine the regions of accumulations of heavy metals, nutrients, pesticides, phthalates and organic matter.

Generally, the overall quality of the nearshore waters of Lake Superior is high and the values of important parameters are well within the limits prescribed by the Ontario Ministry of the Environment for all uses. These waters do not appear to have been adversely affected as yet by the urban and industrial development which has caused significant localized impairment.

INTRODUCTION

The Ministry of the Environment carried out four cruises on the nearshore waters of Lake Superior during the period June 22, 1973 to November 9, 1973. The purpose of the survey was to undertake a systematic monitoring of the entire Canadian shoreline of the lake to determine the quality of water presently available, and to establish base lines against which future improvement or deterioration can be measured as additional shoreline development takes place. With this purpose in mind, the present study was developed to not only satisfy the information requirements of the Ministry, but also to provide input to the current study of lakes Huron and Superior by the International Reference Group on Upper Lakes Pollution (International Joint Commission).

The nearshore program generated extensive information on physical, chemical and bacteriological aspects of water quality on 67 stations along the north shore of the lake, from Whitefish Bay to Thunder Bay in a band generally ranging up to 8 kilometers offshore. In addition to this, several intensive water quality surveys were undertaken in the following embayment areas: Peninsula Harbour, Jackfish Bay, Black Bay, Nipigon Bay, Thunder Bay and Pine Bay.

The intensive studies in the local areas were designed to determine the effects of the municipal and industrial water use in the adjacent land areas and also to delineate the areas of differing water quality in the embayments resulting from the inflow of tributary streams and various other water sources (storm sewer overflow, surface drainage, etc.).

Water quality parameters analyzed for both extensive and intensive

sampling programs were: dissolved oxygen, suspended and dissolved solids, conductivity, turbidity, nitrogen, phosphorus, phenols, alkalinity, chloride, sulphate, pH, heavy metals, dissolved silica, water temperature, chlorophyll a, total and fecal coliforms and fecal streptococci.

Bottom surficial sediments and cores were taken to determine the nature of lake productivity, nutrients present in the sediment, and physical and chemical nature of the sediment. Heavy metal and trace organic levels were also analyzed.

Earlier investigations of Lake Superior using a variety of methods and techniques are reported in the literature. Beeton (1959) investigated the seasonal variation of major ions in the open waters of the lake by collecting data over several years. Putnam and Olson (1960, 1961) studied a limited area of the lake over an extended period of time. The Great Lakes Institute, University of Toronto (Great Lakes Data Report, 1963) and the Canada Centre for Inland Waters (Weiler and Chawla, 1969) undertook extensive studies of the whole lake to appraise trends and changes in the composition of Lake Superior waters. Adams, Jr. (1972) examined the long term changes and seasonal variations in certain physico-chemical properties of Lake Superior waters by comparing his data with historical information. Schelske and Roth (1973) gathered limnological data from a cruise in July 1970 and reported on chemical conditions then which agreed with the earlier findings of Weiler and Chawla. A summary of the past studies conducted on Lake Superior is presented in Table 1.

DESCRIPTION OF THE STUDY AREA

HYDROLOGY

Lake Superior, the largest of the St. Lawrence Great Lakes, is approximately 610 km long, 260 km wide and of 440 m maximum depth. The total surface area of the lake is 82,360 km², of which 28,750 km² is in Canada; the total volume of the lake is 12,220 km³. About 81,600 km² of Canadian land drains into Lake Superior. This drainage basin area includes portions of the Algoma, Sudbury and Thunder Bay districts of Ontario. The major river inflows on the Canadian side are the Kaministiquia River, Long Lac Diversion, Magpie River, Michipicoten River, Montreal River, Nipigon River and White River. The St. Marys River is the outlet for Lake Superior.

PHYSIOGRAPHY

Lake Superior collects water from precipitation on its surface and also from precipitation within the drainage basin. It has been suggested (Beeton, 1965 and Kramer, 1964) that the chemical composition of Lake Superior water resembles that of rainwater since the drainage into the lake has little time to react with resistant pre-Cambrian metamorphic rocks that underly the drainage basin. Most of the basin consists of pre-Cambrian igneous and metamorphic rock. The topographic map of the lake bottom along the Canadian shore from the St. Marys River to Pigeon River has been constructed by Mothersill (1971a, 1971b, 1972).

WATER USAGE

Information regarding the usage of waters of the study area for municipal and industrial consumption, for recreation, fish propagation and transportation, and for the disposal of sewage, industrial and other wastes was obtained from the records of the Ministry and other agencies. A description of water

uses is presented in later sections where results are discussed for each local area and nearshore waters.

SURVEY PROCEDURES

The selection of sampling stations for this study was based on a monitoring grid established by the Ministry of the Environment in its water quality surveys of nearshore water of Lake Superior in 1967 and 1968. Information concerning the sources of waste discharges, type of wastes, treatment provided, flow quantities and variations, location and size of outfalls helped in establishing the sampling stations in the receiving waters of the local effects studies. These stations were chosen in such a way as to include significant sources of pollution and enable the collection of data showing trends of degradation and recovery from effects of waste discharges. In the local studies, a number of nearshore coastal sampling stations which were not suspected to be polluted were included to provide a background. The nearshore stations were intended to delineate areas of high water quality from the areas of water quality impairment resulting from tributary water influx and other water uses. The area covered by the water monitoring cruises of 1973 is shown in Figure 1.

During each survey, vessel positioning was accomplished with the aid of radar and depth sounding. At each station, grab samples were collected at different depths after completing a bathythermograph cast. Samples were taken at surface (1.5 m from the surface), at mid-thermocline and at mid-hypolimnion. Reversing thermometer temperatures were noted at each sampling level and water transparency was measured with a Secchi disc. Since certain properties and concentrations of materials in waters may change with time, where practicable, determinations of these were made immediately after the collection of the sample. These were pH, dissolved oxygen and

the total alkalinity. Determinations of pH with a battery operated Ecolab Model 102D pH meter, dissolved oxygen concentration by the azide modification of the iodometric method and total alkalinity by titration with a standard acid ($0.2\text{ N H}_2\text{SO}_4$) using methyl orange indicator, were made on each sample immediately after recovery. In addition, qualitative observations were made as to colour, odour, turbidity and appearance of the water samples. Quantitative determinations for dissolved minerals and nutrients, colour, turbidity, conductivity, phenols, coliform organisms and certain other special constituents were made in the laboratory. For nutrient determinations, samples were frozen in polyethylene bottles by using dry ice in the field and shipped to Toronto laboratory for analysis. For bacteriological analyses, sampling schedules were so arranged that the maximum time elapsing between collection of samples and delivery to a mobile laboratory, for examination, never exceeded 12 hours. Samples for bacteriological examination were collected by means of a sampler which permitted the filling of a sterile rubber bulb without contamination. These were immediately cooled by ice for transportation to the shore laboratory.

Water samples were taken, using 3-litre capacity Kemmerer (Foerst Scientific) brass water collection bottles (surface samples) and 2-litre Nansen bottles (depth samples). Samples for chlorophyll analysis were filtered (Millipore-aperture size $1.25\text{ }\mu$) onboard and the filters returned on ice to the laboratory.

Grab samples of sediments were taken at selected stations using a model 860 Shipek grab (Hydro Products Inc., San Diego, Calif., U.S.A.).

For core samples, a Phleger model 840A corer (Hydro Products) was used. Sediment samples were shipped to the Toronto laboratory in a sealed glass container for analyses of heavy metals, pesticides, and persistent organic compounds.

PRESENTATION OF DATA

The average values (all cruises) for the chemical parameters on water samples from the five local areas and the inshore areas of Lake Superior are listed in Table 2 along with the standard deviations and the range of values for each parameter.

Figures 2 and 3 show comparisons of the water quality parameters of the inshore lake areas with those obtained for the embayments. Selected locations in the fringe areas of each embayment studied were statistically tested to determine if there were significant differences between them and the adjacent nearshore stations in the mean values over the study period for the following parameters: conductivity, dissolved silica, phenols, chlorophyll a, dissolved oxygen, total nitrogen and total phosphorus. The stations chosen for testing were selected on the basis of geographical locations, i.e. when it was felt that a particular station was located in an area which could be classified either as "nearshore" or "embayment". These locations of undetermined character were Stations 21, 22, 27, 32, 33, 34, 40, 41, 43, 44, 91, 124, 308, 312, 319, 527, 556, 557, 558, 559, 560, 561 and 578.

The statistical testing took the form of an F-test, as follows:

$$F_{r-1, N-r} = \frac{(\bar{X}_1 - \bar{X}_2)^2}{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}} \times \left[\frac{1}{n_1} + \frac{1}{n_2} \right]$$

where: \bar{X}_1 = mean concentration (s) being compared with other mean
annual concentration (s), i.e. \bar{X}_2
 \bar{X}_2 = mean concentration (s) being compared with concentrations (s),
i.e. \bar{X}_1
 n_1 = number of samples included in \bar{X}_1
 n_2 = number of samples included in \bar{X}_2
 S_1 = standard deviation associated with \bar{X}_1
 S_2 = standard deviation associated with \bar{X}_2
 r = number of populations sampled
 N = total number of samples

The test was performed for each parameter individually. For any particular parameter, those locations exhibiting no significant differences in mean values from the mean concentrations of other individual adjacent nearshore stations were classified as being "nearshore" for that parameter, while those showing significant differences were subsequently tested against grouped means taken from a number of known "nearshore" stations in the vicinity.

Figures 4 to 14 are provided to document some of the more significant examples of areal differences in water quality.

Figures 4, 5 and 6 exhibit the areal distribution of the mean concentrations of total phosphorus, chlorophyll a and Secchi disc readings in the surface waters of nearshore areas of Lake Superior.

Figures 7 and 8 present the areal distribution of the mean concentrations in Thunder Bay for chlorophyll a and total phosphorus, respectively.

Figure 9 shows the same for the mean Secchi readings in Black Bay and Figure 10 shows the areal distribution of the mean phenol concentrations in Jackfish Bay.

Figures 11 and 12 represent the distribution of heavy metals (Pb, Hg, Zn, Cd, Ni, Fe, Cr, Cu) in the surficial sediments taken from the nearshore areas of Lake Superior.

Figures 13 and 14 exhibit the distribution of mercury in sediments taken from Peninsula Harbour and the characteristics of the sediment core respectively.

DISCUSSION OF RESULTS

WATER QUALITY FINDINGS

In the following section the water quality findings are discussed. It must be acknowledged that comparisons among the local areas and with the nearshore waters were done with caution, since the depth of study in each area was dictated primarily by previous knowledge of the extent of impairment, and as a result the means and standard deviations based on sampling stations much closer to a source of pollution in one area could not be directly compared with those based on virtually unpolluted stations in other areas where the source of pollution was relatively farther away. The significance of the data in demonstrating impairment was not, however, influenced by such variations in sampling.

Dissolved Oxygen

The dissolved oxygen level is perhaps one of the most important measures of water quality because it reflects the suitability of the resource for the support of aquatic life and determines whether conditions exist for accelerated regeneration of nutrients and heavy metals from sediments.

The range of percentage saturation of oxygen found in the surface waters of nearshore areas was 85-151. No significant depletion over surface levels was noted on depth samples. Since oxygen determinations were most often made at maximal diurnal temperature and illumination, one expects slight supersaturation due to photosynthesis. The above noted minimum saturation was observed at station 100 in Whitefish Bay while the minimum concentration of 8.6 mg/l occurred at station 319 at the Nipigon Strait outlet of Nipigon Bay.

The percent saturation values in the inner harbour of Thunder Bay

were generally found to be inversely proportional to the distance from waste sources. The lowest oxygen level (40% saturation, 3.2 mg/l) was encountered in the north section of the harbour which is influenced by the waste input from the pulp and paper mill operations in the area.

In Jackfish Bay, oxygen-consuming materials from a kraft mill were found to suppress oxygen levels to 6.0 mg/l (61% saturation) at the mouth of Blackbird Creek which carries the wastewaters to the bay.

In general, the nearshore waters and most embayment areas of Lake Superior showed excellent dissolved oxygen content. Only in the inner harbour area of Thunder Bay were oxygen values below the level considered necessary for the support of the cold-water fishery. The comparison of the nearshore areas with the embayments is shown in Figure 2.

Transparency

Materials in suspension are responsible for influencing the water quality by restricting the penetration of sunlight and thereby affecting the biological environment. By reducing light penetration, turbidity tends to inhibit growth of phytoplankton and other algae, where nutrient levels would otherwise be sufficient to produce nuisance growths. On the other hand, nutrients associated with resuspended bottom sediments may stimulate algal growth. In addition to its ecological importance water clarity is a prime consideration in determining the aesthetic value of a water resource. The nearshore waters of Lake Superior exhibited the highest clarity of the areas studied as reflected by a mean Secchi depth of 8.5 m with a range of 0.5 to 15 m. Black Bay was found to be the most turbid of all areas

surveyed with an average Secchi depth of 2.3 m. A comparison among all areas studied is shown in Figure 2.

When one examines results for Secchi disc readings in the nearshore waters as shown in Figure 6, it is seen that the only areas affected by low transparency are portions of Batchawana Bay, Nipigon Bay and Thunder Bay. The Secchi readings for Black Bay are shown separately in Figure 9. While the turbidity observed in Black Bay and Batchawana Bay is attributable to the natural resuspension of bottom sediments by wave energy in these shallow waters, the lower transparency in Thunder Bay and to a lesser extent in Nipigon Bay can be traced to urban and industrial sources of suspended solids.

Nutrients

Nutrients are responsible for the productivity of a lake. Man's activities accelerate the natural introduction of many substances into the lakes which can result in conditions of increased productivity which often lead to nuisance algal growth. The substances responsible for these conditions are carbon, nitrogen and phosphorus and a number of other substances which are required in very small quantities, such as Mn, Fe, S, etc. Among the nutrient forms examined during this study are dissolved P, total P, $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$ and dissolved SiO_2 .

As evident from Table 2, the total P ranged from 1-37 ug/l in the nearshore waters with an average value of 6 ug/l. Total P was much higher in Thunder Bay Harbour (24 ug/l) than in any other zones. The average value of 33 ug/l for Pine Bay is not considered realistic in view of the

extremely small number of samples used in the calculation. The total phosphorus values in Thunder Bay ranged from 6 to 98 ug/l with high average values in the inner harbor. The highest recorded value of 98 ug/l occurred near the industrial and municipal outfalls. Phosphorus compounds added to a local area from municipal and industrial effluents stimulate growth of aquatic plants. The increases may occur in phytoplankton or in bottom vegetation, depending upon such factors as depth, transparency, temperature, etc. At certain threshold concentrations of P, the abundance of aquatic plants reaches nuisance proportions (Sawyer, 1947). Although this threshold concentration of 20 ug/l was exceeded, no phytoplankton growth was noticed in the area. However, without a simultaneous biological study, it was not possible to say whether abundances of diatoms were actually observed or any correlation with phosphorus existed.

Figure 4 shows the areal distribution of total phosphorus in the nearshore waters. It can be seen from the figure that in the zone between Whitefish Bay and the entrance of the eastern channel of Nipigon Bay, the total P concentrations were less than 7 ug/l except for a portion of Batchawana Bay and a small area near Marathon where higher values were observed. Near Rossport, the phosphorus concentration was higher than the general area, and portions of Nipigon Bay and the mouth of the western channel exhibited still higher values. The zone between the western channel of Nipigon Bay and Thunder Bay Harbour showed the same quality as Rossport area. Figure 8 shows the concentrations of phosphorus in Thunder Bay area. This has a marked contrast with the overall nearshore waters of

Lake Superior. The nearshore region of Thunder Bay was defined by the concentrations of gradients from the shore to the lake. This gradient levelled out at a distance of approximately 5 km from the shore and the water quality in terms of total P became identical with the general quality of nearshore waters of Lake Superior.

The mean surface concentrations of dissolved phosphorus, total N, nitrate-N, ammonia-N and dissolved silica in the nearshore zone were 2, 310, 190, 16 and 2220 ug/l respectively (Table 2). Soluble phosphorus concentrations were the lowest in nearshore waters compared to any other zones. Total nitrogen in all the zones except Thunder Bay were rarely above 300 ug/l, the amount reported to be necessary for the production of nuisance blooms of algae (Sawyer, 1947). Again, Thunder Bay stations showed high values near the municipal and industrial outfalls. However, in the absence of accompanying biological information, the effect of nutrient supply on the activity of the biota cannot be evaluated. In surface water, the presence of ammonia-N is often interpreted to suggest the presence of pollution by sanitary sewage. It is also present in many industrial wastes. Therefore, the higher values for this nutrient in Thunder Bay, Black Bay and Jackfish Bay are consistent with this contention. The other concern about nitrogen in surface waters is that nearly all of it is ultimately oxidized to nitrate, which causes blood disorder of infants. Since Lake Superior water is used by certain municipalities for public water supplies, this factor may become important. However, the levels of nitrate and other nitrogen compounds present in Lake Superior water has a respectable safety factor.

The average concentration of dissolved silica in nearshore waters of Lake Superior was not much different from the averages found in Black Bay and Thunder Bay. The source of silica in lake waters is the geological deposits in the drainage basin. Since silica is used up as a nutrient by certain diatoms, usually lower levels are expected in the surface waters where diatoms are active. As evident from Table 2, the harbour areas at Thunder Bay and Pine Bay have, in fact, higher values of dissolved silica than the nearshore waters. This depletion of silica in nearshore waters can be interpreted as due to the presence of active diatoms in the epilimnion. The probable explanation for the abundance of silica in the surface waters of the bay is that the diatoms requiring silica for growth were absent. However, the level of dissolved silica observed in the nearshore waters compared very well with the earlier studies reported in the literature.

Beeton (1971) compiled the chemical compositions of Lake Superior waters and presented in a tabular form the average values for several parameters, covering the period 1850 to 1963. A comparison of the mean concentrations of nutrients found in this survey with those of earlier studies is presented in Table 3. An examination of the data suggests that the average concentrations of total P and dissolved SiO_2 observed in the present study agrees well. The mean concentration of NO_3^- -N was in reasonable agreement with Schelske and Roth's data, but was somewhat lower than Beeton's findings. It must be remembered, in comparing our data with theirs, that the other authors averaged the concentrations found over lake-wide sampling stations whereas our sampling sites were limited to 8 km from the shore.

Chlorophyll *a*

Chlorophyll *a* levels provide a measure of the standing phytoplankton crop. Average chlorophyll *a* concentrations in the surface waters of the nearshore areas of Lake Superior were found to be 0.8 ug/l with maxima rarely exceeding 2 ug/l at any location. In contrast, in the embayment areas the concentration ranged from 0.4 to 3.8 ug/l with average values of 1.3, 1.5, 1.2 and 1.2 in the inner harbour of Thunder Bay and in Black Bay, Jackfish Bay and Pine Bay respectively. The distribution of chlorophyll *a* in the surface waters of nearshore areas is shown in Figure 5. The distribution clearly shows that all areas have low chlorophyll *a* values with somewhat higher levels in the open waters of Nipigon Bay and Thunder Bay. Figure 7 shows the distribution in the harbour area of Thunder Bay. As is seen from the figure the pattern appears to be the same as for total phosphorus in the bay. Therefore, an attempt was made to find a correlation between the two parameters. A plot of total P against chlorophyll *a*, however, did not show a quantifiable good correlation nor did a plot of chlorophyll *a* against Secchi disc. No estimates of the state of eutrophication in Thunder Bay could be made from chlorophyll *a*, total P, Secchi disc, surface area and depth data, since the observed range in water quality was too narrow.

Total Dissolved Solids and Conductivity

Specific conductance measurements are an excellent way of determining ionic composition of an aqueous system. The ionic species in the dissolved solids contribute towards the conductivity. Beeton and Chandler (1963)

showed a direct relationship between the specific conductivity and the ionic strength of the Great Lakes waters.

During the present study, the nearshore waters of Lake Superior were characterized by low total dissolved solids which averaged 62 mg/l. The embayment areas showed somewhat higher dissolved solids content but did not exceed 105 mg/l. The most significant levels of dissolved solids and resultant high specific conductance were observed in the harbour area of Thunder Bay which receives major waste inputs from industrial and municipal sources. Considerable reduction in the dissolved solids level was observed with increasing distance from the City of Thunder Bay shoreline. In the open waters of the bay the level dropped to 60 mg/l which was the same as the average for the nearshore waters of Lake Superior.

The conductivity values averaged 97 umho/cm for the nearshore waters of Lake Superior which agreed very well with other authors who measured conductivity in the open lake. Figure 2 shows the comparison of local areas with the nearshore waters for conductivity.

Phenolic Substances

The presence of phenolic substances in surface waters may contribute to taste and odour problems in water supplies and are believed to partly contribute to tainting of fish flesh. Kraft mill effluents and inadequately treated municipal wastes are among the most common sources of phenols added to the surface waters. In the Ontario basin of Lake Superior, the principal industry is kraft pulp and paper and as such impairment due to phenol is expected. Since the bleaching agents in the kraft process

contain chlorine dioxide and sodium hypochlorite, it is likely that the effluent from such a process includes chlorinated phenols which in very small quantities can impart off-flavour to fish and add taste and odour to public water supplies. The phenol values determined in this study may include chlorinated phenols which were not analysed separately. Although phenol levels in the receiving waters were not above the fish taste threshold concentrations reported in the literature, some fish samples taken from Thunder Bay and Nipigon Bay have been found to be tainted.

The areal distribution of phenols in Jackfish Bay waters is shown in Figure 10. Phenol levels were higher than the background levels of nearshore waters of Lake Superior up to 3 km from the mouth of Blackbird Creek, which carries kraft mill effluent to the receiving waters of Jackfish Bay. The monitoring data indicated average concentrations of phenolic substances to be 4 ug/l in the inner harbor of Thunder Bay, which is influenced by municipal and industrial discharges.

Other Physico-chemical Parameters and the Bacteriological Data

In the Lake Superior basin, the presence of slowly weathering pre-Cambrian rocks makes it difficult for the drainage waters to dissolve the chemical constituents and therefore, the mean alkalinity is rather low. The average total alkalinity of 39 mg/l for nearshore waters is consistent with the findings of other authors (Beeton, 1971; Schelske and Roth, 1973). The only area to show somewhat higher alkalinity in this survey was Thunder Bay and is attributed to population density and industrial development in this region. Values of pH ranged from 7.7 to 8.3 in the nearshore waters.

There was no noticeable seasonal variation of alkalinity and pH. Adams, Jr. (1972) has correlated both alkalinity and pH with water temperature of Lake Superior. Weiler and Chawla (1968) found a seasonal variation of alkalinity and pH in Lake Erie and correlated it with the productivity of the lake. No such correlation could be established with the limited data that was available for Lake Superior.

Bacterial levels measured in the nearshore waters during the survey were found to be within the Ministry's criteria for public water supplies. The three parameters measured: total coliform, fecal coliform and fecal streptococci showed elevated levels in Peninsula Harbour and Jackfish Bay compared to control stations in non-industrialized nearshore areas of Lake Superior. In Peninsula Harbour, the total and fecal coliform counts were within this Ministry's guidelines; but the fecal streptococci counts exceeded these criteria on all stations. No trend was apparent in respect to population density of fecal streptococci with distance from the outfall. Bacterial population in Jackfish Bay was highest at the mouth of Blackbird Creek which carries the kraft mill effluents to the receiving waters of the bay. A general decrease in densities toward the open waters of Jackfish Bay was observed. A large variability in bacterial counts over a few hours made it impossible to estimate the condition of the bay in regard to recreational uses. A similar survey carried out in Thunder Bay inner harbour during August 1970 suggested that the bacteriological data did not meet the accepted microbiological criteria for swimming and bathing.

SEDIMENT CHARACTERISTICS

Mothersill (1971a, 1971b, 1972) has summarized the surficial geology of the Canadian shoreline from the St. Marys River to Pigeon River. Nussmann (1965) investigated the trace elements in the sediments of Lake Superior. Grab samples of sediments along the Canadian shoreline were examined in the present study. Nutrients, heavy metals, percentage loss on ignition, phthalates, PCB and pesticides were determined in the nearshore sediments. Table 4 lists the levels of these parameters in specific locations of the lake sampled. The sampling locations are shown by station numbers in Figure 1. A brief description of the sediment sample is also included in Table 4. Figures 11 and 12 show the distribution of heavy metals in the surficial sediments.

Pollutants such as pesticides may be absorbed under field conditions by soil aggregates and transported to lakes as sediments. The possibility that changes in bottom fauna usually attributed to increasing oxygen demand may actually be caused by pesticides has been suggested. However, it is not known what types of pesticides and in what levels would their presence be harmful to bottom fauna. Also, there is lack of information on what effects do benthic animals and plants have on changing the chemical composition of sediments. Pesticide analysis in Lake Superior sediments did not reveal the presence of lindane, heptachlor, aldrin, heptachlor epoxide, thiodan, dieldrin or endrin. Only low levels of DDE, DDD and DDT were found in these sediments. These levels were considered acceptable.

During the development of a lake, algal organisms are sedimented to the bottom along with other organic and inorganic materials. Bacteria present at the bottom decompose the organic material, but a substantial portion may remain there and with the build up of sediments over the years, they may never be exposed to the overlying waters. The quantity of organic P and N, and other chemical features, give an approximation of the productivity of the lake. The low nutrient levels found in these sediments suggest a poor productivity of Lake Superior. Sediment samples collected in Thunder Bay and Jackfish Bay exhibited slightly higher levels of total phosphorus and total nitrogen than the background levels in sediments of nearshore waters of Lake Superior. It is, however, unlikely that a release of nutrients occurs from the sediments to the overlying waters since the oxygen levels are near saturation. Accumulations of decomposing bottom deposits were found in some of the sampling locations in Thunder Bay and Jackfish Bay. These deposits consisting of wood fibres, clay and silt contained a maximum of 5% volatile material.

PCB levels in the nearshore sediments were found to be extremely low. Out of 28 samples, only three had measurable levels, seven showed trace amounts below the sensitivity limit of the test and 18 did not have any PCB at all. The PCB's are not soluble in water but are extremely persistent in the environment. They are dangerous and can be transmitted through the food chain. The measureable levels occurred in the vicinity of Marathon where a maximum concentration of 250 ug/kg was found.

The heavy metal analyses for sediment samples collected in the nearshore waters included determinations of mercury, lead, copper, chromium,

cadmium, zinc, nickel and iron. Various workers have demonstrated a requirement of aquatic plants for these substances in low concentrations. In higher concentrations, however, they become toxic to the aquatic system and eventually to man. There is lack of information on the levels at which heavy metals can affect the aquatic environment.

From an examination of Figures 11 and 12, it is evident that the sediments near localized centres of population and industrialization showed somewhat higher levels of heavy metals than the non-industrialized areas. The heavy metal levels in the undeveloped areas reflect the natural levels due to soil weathering and geochemical processes, although it is possible that they may be affected by the transport of sediment from the industrial areas.

Significant mercury contamination of sediments was observed in Peninsula Harbour, and is attributed to past mercury losses from a chlor-alkali plant in the area. The sediment sampling locations in this special study and concentrations of mercury are shown in Figure 13. The greatest contamination found in this study was in Jellicoe Cove near the main mill sump overflow of the chlor-alkali plant. Concentrations of 38.3 mg/kg and 31.9 mg/kg were detected at distances from the outfall of 180 and 480 metres respectively. The distribution pattern of high concentrations followed a line from the outfall westward to Hawkins Island, where a decrease in concentration from 38.3 mg/kg near the outfall to 10.3 mg/kg occurred at a distance of 500 m from the outfall. This pattern then divided into a northern and southern component. The northern component reached into

Beatty Cove where a concentration of 9 mg/kg was detected. The southern component extended into the somewhat larger area between Hawkins Island and the peninsula. Concentrations between these two landmarks range from 0.515 to 5.8 mg/kg with a mean of 2.8 mg/kg. Unfortunately, the sampling grid in the special study did not extend far enough south of Hawkins Island to reach background levels.

A general relationship may be noted between mercury concentrations and depth of water. The distribution of highest values outlined above is confined to the deeper parts of Peninsula Harbour - areas greater than 27 m in depth. In contrast, the relatively shallow, inner region of the harbour which has a mean depth of 9 m was affected to a much lesser degree having a mean mercury concentration of 0.24 mg/kg. Of course, this relationship does not hold true for the immediate vicinity of the outfall, where high concentrations would be expected.

The predominant sediment type associated with the deeper, heavily contaminated area of Peninsula Harbour is silt. By comparison, sediments in the shallow, inner harbour consisted mainly of fine sand.

The areas outside Peninsula Harbour covered by this special study were the portion of Lake Superior immediately south of the peninsula and the area northwest of Peninsula Harbour known as Port Munro. Although mercury levels in these areas were lower than inside the harbour, the effect of the outfall was still evident, especially to the south of the peninsula where concentrations ranged from 0.2 to 1.8 mg/kg. The lowest levels were found in and around Port Munro, the range of values for this area being 0.008 to 0.9 mg/kg.

A few core samples were taken in Peninsula Harbour to determine the amount of mercury in each layer of the sediments. It was felt that this may provide an insight into the record of sediment mercury accumulation. Analytical results for core samples are presented graphically in Figure 14. It is evident from the figure that the highest concentrations were restricted to the top 5 cm of the samples. The two cores obtained at Station C-5 gave very different results. The second core was stratified into silt, silt plus clayey sand, and clayey sand. This core agreed well with the result of 18.8 mg/kg obtained from the grab sample for the same station. On the other hand, the first core was rather homogeneous, consisting chiefly of clayey sand with some wood fibres on the top one-half cm. Concentrations found in this core showed a general agreement with the clayey sand segment (10-15 cm portion) of the second core. The core sample obtained at Station 588 which was 180 m from the outfall of the chlor-alkali plant was not consistent with the grab sample obtained at the same location. The first 8 cm of the core sample showed a mercury content of 20 mg/kg whereas the two grab samples composited had a value of 38.5 mg/kg. This discrepancy probably arose from the amount of organic matter contained at the top of the core sample which appeared to dilute the mercury level in that sample. The core sample at Station 591 agreed well in mercury content with the grab samples.

CONCLUSIONS

On the basis of this study and earlier investigations carried out by the Ministry and formerly by the Ontario Water Resources Commission, the following summary of the Ontario nearshore water quality of Lake Superior is presented. The sources of most of the contamination noted here have been identified and abatement programs are either underway or are being formulated.

The nearshore waters of Lake Superior exhibit high clarity and the temperatures are low. Turbidity in Black Bay appears to arise from the shallowness of the bay.

Although it appears that the oxygen-demanding waste input into the harbour areas is not adversely affecting their water quality, the continuing discharge of carbonaceous materials may contribute to water quality deterioration on a long-term basis. Shallow spawning grounds may disappear unless they are guarded against deposition of bottom organic sediments. Dissolved oxygen is quite adequate in the nearshore waters in spite of municipal and industrial BOD waste input.

Bacterial pollution in Peninsula Harbour, Thunder Bay and Jackfish Bay has been identified and Nipigon Bay studies presently being carried out may indicate similar impairment. The nearshore waters meet this Ministry's water supply and recreational use criteria for total coliform, fecal coliform and fecal streptococci.

Nutrient concentrations in the nearshore waters indicate that these waters are similar to the oligotrophic nature of the open lake. In certain

local areas, e.g. Thunder Bay, the concentrations are somewhat higher, but the oxygen content and temperatures are such that algal productivity is not presently a problem.

There is no heavy metal pollution in the nearshore waters. Therefore, the absence of natural ligands, which bind the excess metals, does not pose a problem in Lake Superior. Unacceptable levels of mercury have been found in fish taken from Thunder Bay and Peninsula Harbour and accumulations of this metal in the sediments of both areas may provide a continuing threat to the biota. During recent years, the mechanisms for the transfer of metallic mercury from bottom sediments to the aquatic food chain through methylation by sediment bacteria have received a great deal of attention from several workers. The release of water-soluble methyl mercury from the sediments to overlying waters in these two areas can be dangerous for the food chain.

Total dissolved solids and conductivity in the nearshore waters are low and they do not appear to be accumulating, but in the face of further population and industrial growth these environmental factors may change. Suspended solids are virtually absent except in the harbour areas and no progressive build-up in the concentrations of any persistent chemical has been noted.

Generally, the overall quality of the nearshore waters of Lake Superior is excellent and the concentrations of important environmental factors are well within the limits prescribed by the Ontario Ministry of the Environment for all uses.

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TABLE 1: Past Studies in Lake Superior

Reference	Kind of Data	Years of Observation
Beeton et al. (1959)	Limnological	1952, 1953
Putnam & Olson (1960, 1961)	Nutrients, Productivity	1959, 1960
Great Lakes Inst. (1963)	Data Report	1960
Weiler & Chawla (1969)	Physico-chemical properties	1968-69
Schelske & Roth (1973)	Limnological	1970

TABLE 2: LAKE SUPERIOR - 1973 - PARAMETER SUMMARY BY AREAS

<u>Areas</u>	<u>Nearshore</u>	<u>Thunder Bay</u>	<u>Black Bay</u>	<u>Jackfish Bay</u>	<u>Pine Bay</u>	<u>Peninsula Harbour</u>
<u>Parameters</u>						
Total P (mg/l)	.006 ± .004 (254)* .001 - .037**	.024 ± .011 (54) .006 - .098	.012 ± .022 (24) .003 - .052	.018 ± .017 (14) .004 - .070	.033 ± .026 (4) .015 - .070	.006 ± .002 (9) .004 - .010
Diss. P. (mg/l)	.002 ± .002 (258) .001 - .020	.005 ± .003 (47) .001 - .017	.006 ± .008 (24) .001 - .040	.008 ± .003 (14) .001 - .040	.042 ± .008 (4) .004 - .020	.002 ± .001 (9) .001 - .004
Total N (mg/l)	.31 ± .05 (271) .15 - .49	.41 ± .12 (53) .20 - .88	.26 ± .05 (24) .19 - .37	.32 ± .02 (14) .27 - .45	.41 ± .35 (4) .21 - .94	.28 ± .02 (9) .25 - .31
Diss. Silica (mg/l)	2.2 ± .25 (265) 0.8 - 3.6	2.8 ± .16 (10) 2.2 - 3.5	2.2 ± .07 (24) 2.0 - 2.6	No Data	3.8 ± 2.8 (4) 2.2 - 8.0	No Data
O ₂ Sat. (%)	103 ± 7 (268) 85 - 151	81 ± 15 (75) 40 - 123	104 ± 6 (48) 91 - 113	93 ± 8 (14) 61 - 108	114 ± 6 (4) 108 - 121	105 ± 5 (9) 99 - 115
Chloro a (ug/l)	0.8 ± .4 (275) 0.2 - 3.5	1.3 ± .6 (93) 0.4 - 2.8	1.5 ± .4 (24) 1.0 - 2.8	1.2 ± 1.1 (7) 0.6 - 3.8	1.2 ± .2 (4) 0.9 - 1.4	No Data
Conductivity (umhos/cm)	97 ± 4 (265) 83 - 131	109 ± 9 (90) 94 - 161	No Data	153 ± 39 (14) 94 - 363	108 ± 13 (4) 100 - 127	110 ± 9 (9) 103 - 133
Secchi Depth (m)	8.5 ± 2.5 (284) 0.5 - 15.0	3.0 ± 1.0 (90) 0.5 - 6.0	2.5 ± 0.2 (24) 1.5 - 4.0	2.5 ± .5 (14) 0.5 - 6.0	4.0 ± 5.0 (3) 0.5 - 9.5	3.0 ± .5 (9) 2.5 - 4.5
Diss. Solids (mg/l)	61.7 ± 16.7 (129) 7.0 - 110.0	92.7 ± 24.6 (30) 60.0 - 150.0	85.4 ± 24.9 (12) 55.0 - 150.0	104.3 ± 42.1 (14) 50.0 - 300.0	63.3 ± 11.5 (3) 50.0 - 70.0	No Data
Nitrate (mg/l)	.19 ± .03 (273) .07 - .27	.13 ± .07 (55) .01 - .26	.06 ± .01 (24) .04 - .15	.13 ± .03 (14) .02 - .19	.06 ± .03 (4) .01 - .08	.16 ± .01 (9) .15 - .17
Ammonia (mg/l)	.02 ± .01 (271) .01 - .10	.02 ± .01 (53) .01 - .08	.03 ± .02 (24) .01 - .07	.07 ± .06 (11) .01 - .20	.03 ± .01 (4) .02 - .04	.01 ± 0.0 (9) .01 - .01
Kjeldahl N (mg/l)	.12 ± .05 (276) .03 - .40	.29 ± .14 (49) .10 - .84	.18 ± .05 (24) .10 - .26	.18 ± .03 (14) .09 - .40	.35 ± .38 (4) .13 - .92	.12 ± .02 (9) .10 - .15
pH	8.1 ± 0.9 (28) 6.1 - 8.5	7.6 ± 0.1 (10) 7.0 - 8.3	No Data	No Data	No Data	No Data
Phenols (ug/l)	3.3 ± 5.2 (268) 0 - 50	6.4 ± 3.2 (9) 2 - 15	1.2 ± 0.8 (24) 0 - 4	36.1 ± 18.3 (14) 4 - 155	5.0 ± 1.2 (4) 4 - 6	2.5 ± 1.6 (8) 0 - 6
Water Temp. (°C)	13.0 ± 4.0 (280) 4.0 - 23.0	14.5 ± 4.5 (124) 7.0 - 20.0	19.0 ± 0.5 (48) 14.5 - 22.0	11.5 ± 1.0 (14) 9.0 - 16.5	17.0 ± 1.0 (4) 16.0 - 18.5	10.8 ± 1.0 (9) 9.5 - 13.0
Alkalinity (mg/l)	39 ± 3 (231) 25 - 52	42 ± 19 (70) 33 - 87	44 ± 6 (45) 34 - 53	47 ± 10 (14) 40 - 80	45 ± 9 (4) 37 - 51	40 ± 3 (9) 37 - 43

* - Mean ± Standard Deviation (Sample Size)

** - Minimum Value - Maximum Value

TABLE 3: Comparison of Average Nutrient Concentrations of Present Study
with Earlier Studies on Lake Superior

<u>Nutrients</u>	<u>Present Study</u>	<u>Schelske (1973)</u>	<u>Beeton (1972)</u>
Total P (ug/l)	6	-	5
Nitrate-N (mg/l)	0.19	0.25	0.52
Dissolved SiO ₂ (mg/l)	2.22	2.28	2.1

TABLE 4: Data for Sediment Samples from Lake Superior

Station No.	Total P mg/g	Total N mg/g	Percentage Loss on Ignition	PCB ug/kg	DDE ug/kg	DDD ug/kg	DDT ug/kg	Diethyl Hexyl Phthalate mg/kg	Description of Sediment Sample
556	0.68	1.4	5.2	X	2.1	0.6	0.5		Grey-brown silt containing small lumps of clay
558	0.50	<0.5	2.0	trace	0.9	0.9	0.6	1.1	Silty sand, dark brown in colour, no odour noted
559	0.28	<0.5	0.68	X	X	X	X		Sand
562	0.66	1.4	5.4	trace	3.2	2.7	1.3		Silt, grey-brown in colour
561	0.75	1.2	5.1	X	1.2	1.3	0.5	0	Brown silt
001	0.50	0.8	3.7	X	4.2	2.7	1.1		Sandy silt, dark brown, small lumps of clay
005	0.20	<0.5	0.57	X	trace	X	X	0	Sand
011	0.64	<0.5	0.74	X	trace	X	X		Fine sand
013	0.60	<0.5	1.5	X	trace	X	X		Top 3 cm-coarse sand and gravel, below that, very fine clay
0016	0.50	<0.5	1.4	X	0.6	X	X	0.3	Top 1-2 cm silt, rest is light brown clay
20	0.30	<0.5	2.4	12	X	X	X		Dark grey silt
22	0.50	<0.5	2.2	250	X	X	X		Very fine sand (silty) grey brown
24	0.60	<0.5	0.71	10	X	X	X	1.5	Coarse red sand - top 2 cm, finer grey sand below that
25	0.47	<0.5	1.0	trace	X	X	X		1st cast-top 1 cm coarse sand, pebbles, gravel & small stones, rest is clay
27	0.55	<0.5	1.0	trace	0.5	X	trace		2nd cast-coarse, pebbles, gravel and small stones
29	0.77	0.5	2.0	trace	0.5	X	trace	0	1st and 2nd casts-clayey sand
32	0.46	<0.5	1.0	X	0.8	0.4	0.6		1st and 2nd casts-very fine clayey sand 2 cm; sandy clay below that
34	0.89	1.9	5.0	X	3.6	3.2	0.8		Coarse sand, gravel-top 2-3 cm, rest is clay
312	0.52	1.1	4.0	X	3.4	2.3	1.0		Very loose (soupy) clay
319	0.57	0.62	2.5	X	0.9	0.7	1.1	0.3	Very loose (soupy) clay
40	0.52	0.30	1.5	X	0.8	0.5	1.0		Loose clay
41	0.53	0.31	2.0	X	0.3	0.5	0.5		1st Cast-top 1-2 cm sand clay with few pebbles, below is fine clay, few thin pieces of bark
43	0.52	0.27	1.5	X	0.4	0.4	0.7		2nd Cast-less sand, no bark
578	0.30	0.50	0.7	X	0.2	0.4	0.6		1 cm of coarse sand on fine clay
44	0.45	1.0	2.0	trace	1.0	0.5	1.0		Top 2 cm coarse sand, below that silty sand
91	1.90	2.1	5.5	trace	7.1	X	4.4	0.6	Top 1-2 cm coarse and medium grain sand, coarse (very) red sand, rest is clay
527	0.49	0.57	2.0	X	X	X	X		2 cm of medium to coarse sand on sandy clay
124	0.35	<0.5	0.9	X	X	X	X	0.2	Silt 0-3 cm, then reddish brown clay
									1st Cast-coarse sand on hard clay; 2nd-coarse sand on sandy silty clay
									Medium grain sand and silty sand.

"X" denotes not detected

"trace" denotes the level was below the sensitivity limit of the test

Sensitivity Limits:

PCB 10 ug/kg; DDD and DDT 0.5 ug/kg; DDE 0.2 ug/kg

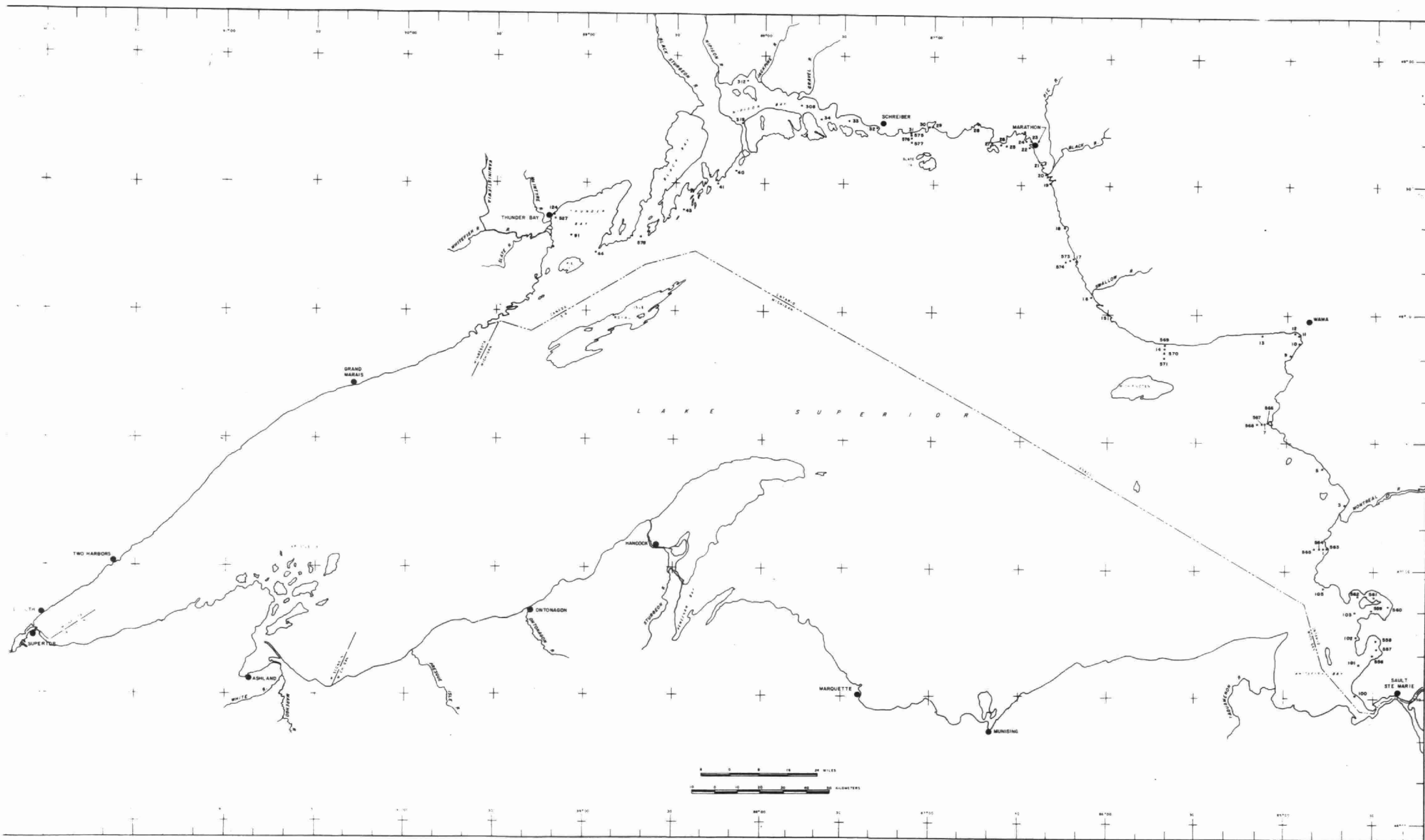
FIGURE LEGENDS

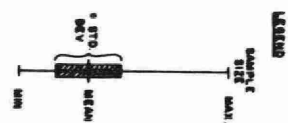
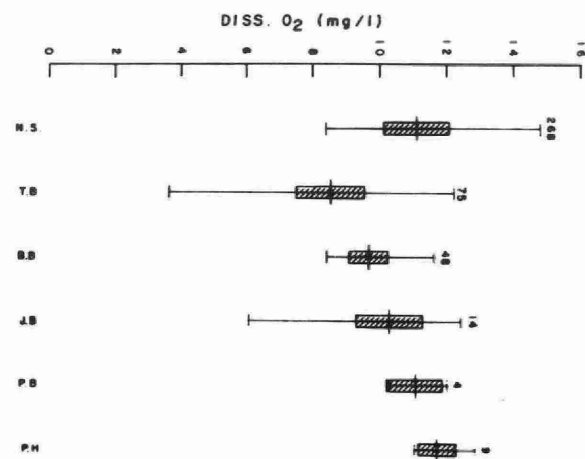
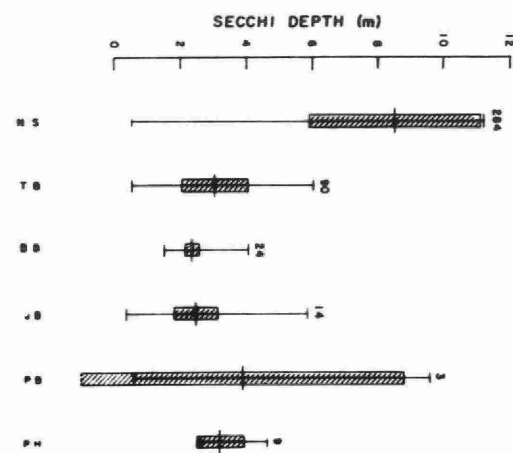
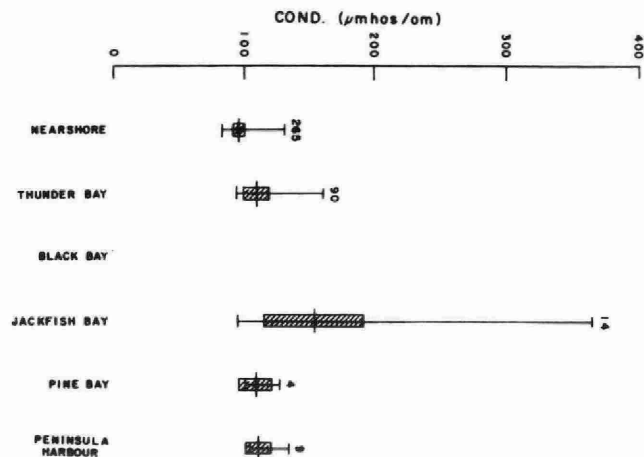
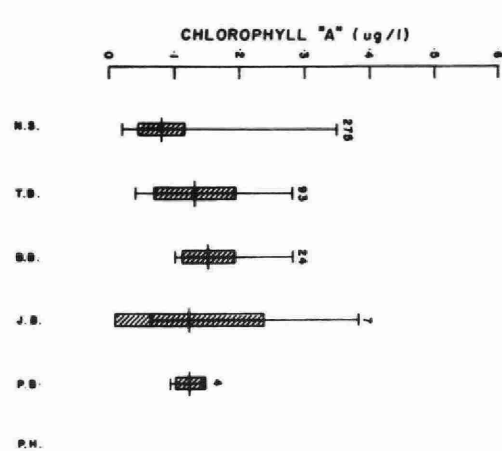
- Figure 1 Index map of sampling sites in Lake Superior.
- Figure 2 Conductivity, dissolved oxygen, Secchi disc and chlorophyll a readings in surface waters by lake areas (N.S.-Nearshore, T.B.-Thunder Bay, B.B.-Black Bay, J.B.-Jackfish Bay, P.B.-Pine Bay and P.H.-Peninsula Harbour).
- Figure 3 Total phosphorus, total nitrogen, dissolved phosphorus and dissolved silica in surface waters by lake areas (N.S.-Nearshore, T.B.-Thunder Bay, B.B.-Black Bay, J.B.-Jackfish Bay, P.B.-Pine Bay and P.H.-Peninsula Harbour).
- Figure 4 Areal distribution of total phosphorus in nearshore surface waters of Lake Superior.
- Figure 5 Areal distribution of chlorophyll a in nearshore surface waters of Lake Superior.
- Figure 6 Areal distribution of Secchi disc readings in nearshore waters of Lake Superior.
- Figure 7 Areal distribution of chlorophyll a in surface waters of Thunder Bay.
- Figure 8 Areal distribution of total phosphorus in surface waters of Thunder Bay.
- Figure 9 Areal distribution of Secchi disc readings in nearshore waters of Black Bay.
- Figure 10 Areal distribution of phenol in surface waters of Jackfish Bay.
- Figure 11 Heavy metals distribution in the surficial sediments occurring within the nearshore zone of Lake Superior by sampling locations (Ni, Fe, Cr, Cu).

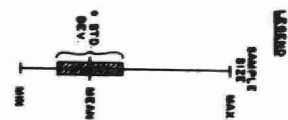
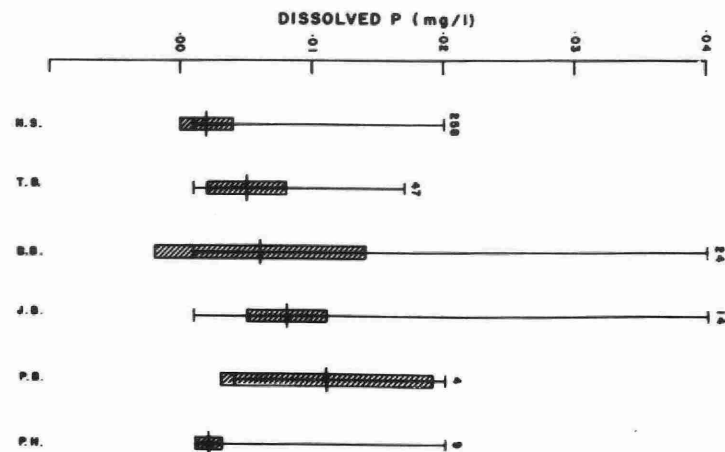
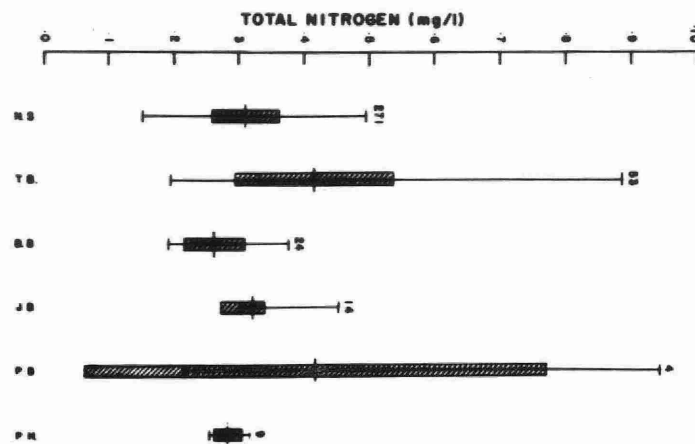
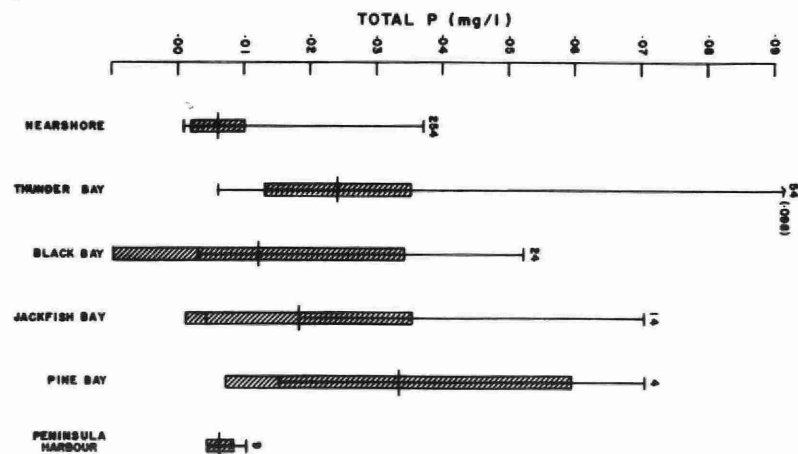
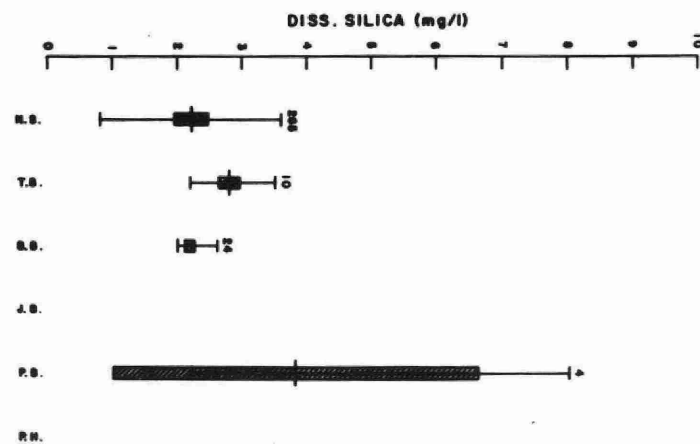
Figure 12 Heavy metals distribution in the surficial sediments occurring within the nearshore zone of Lake Superior by sampling locations (Pb, Hg, Zn, Cd) .

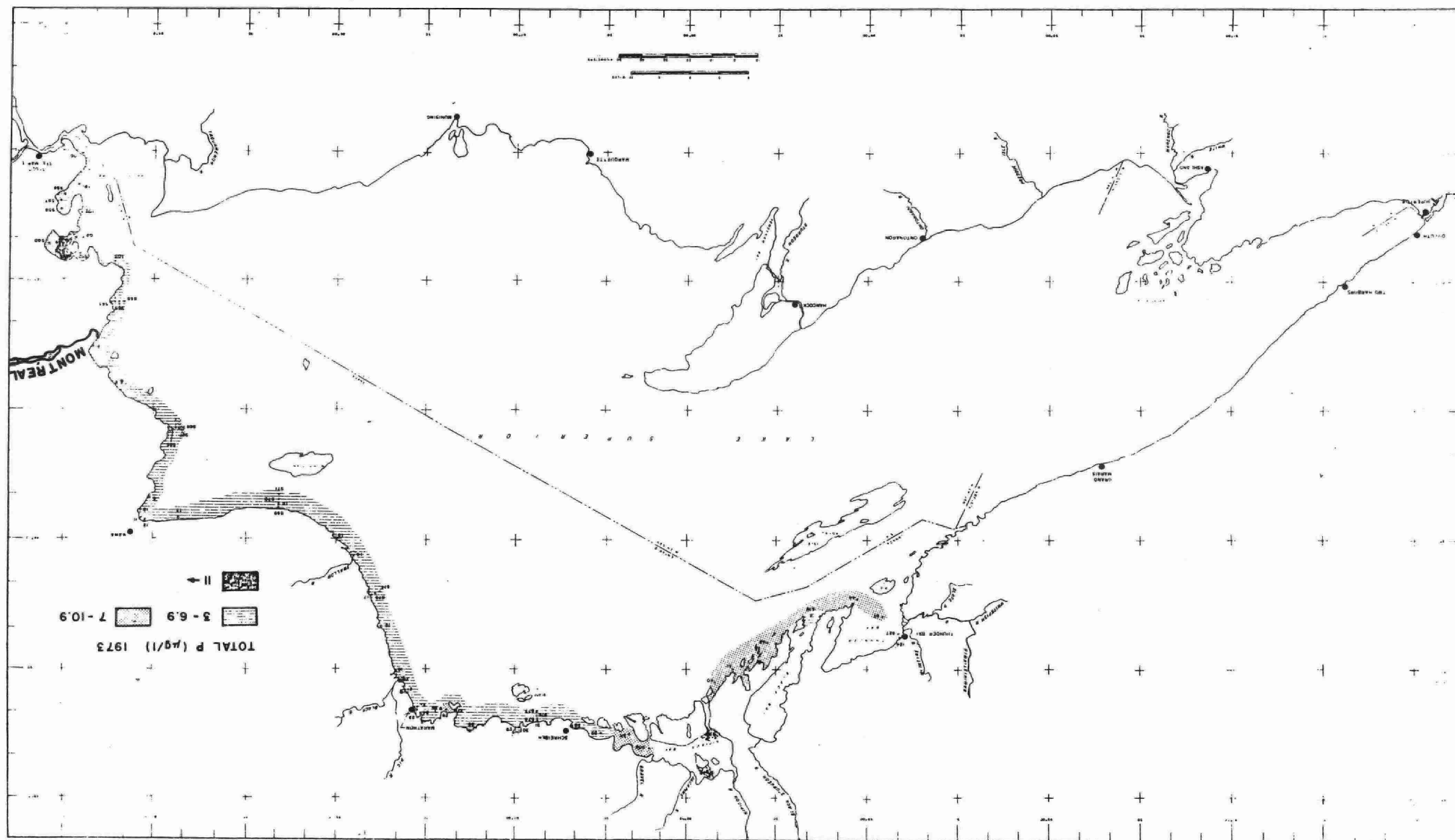
Figure 13 Distribution of mercury in sediment grab samples taken from Peninsula Harbour .

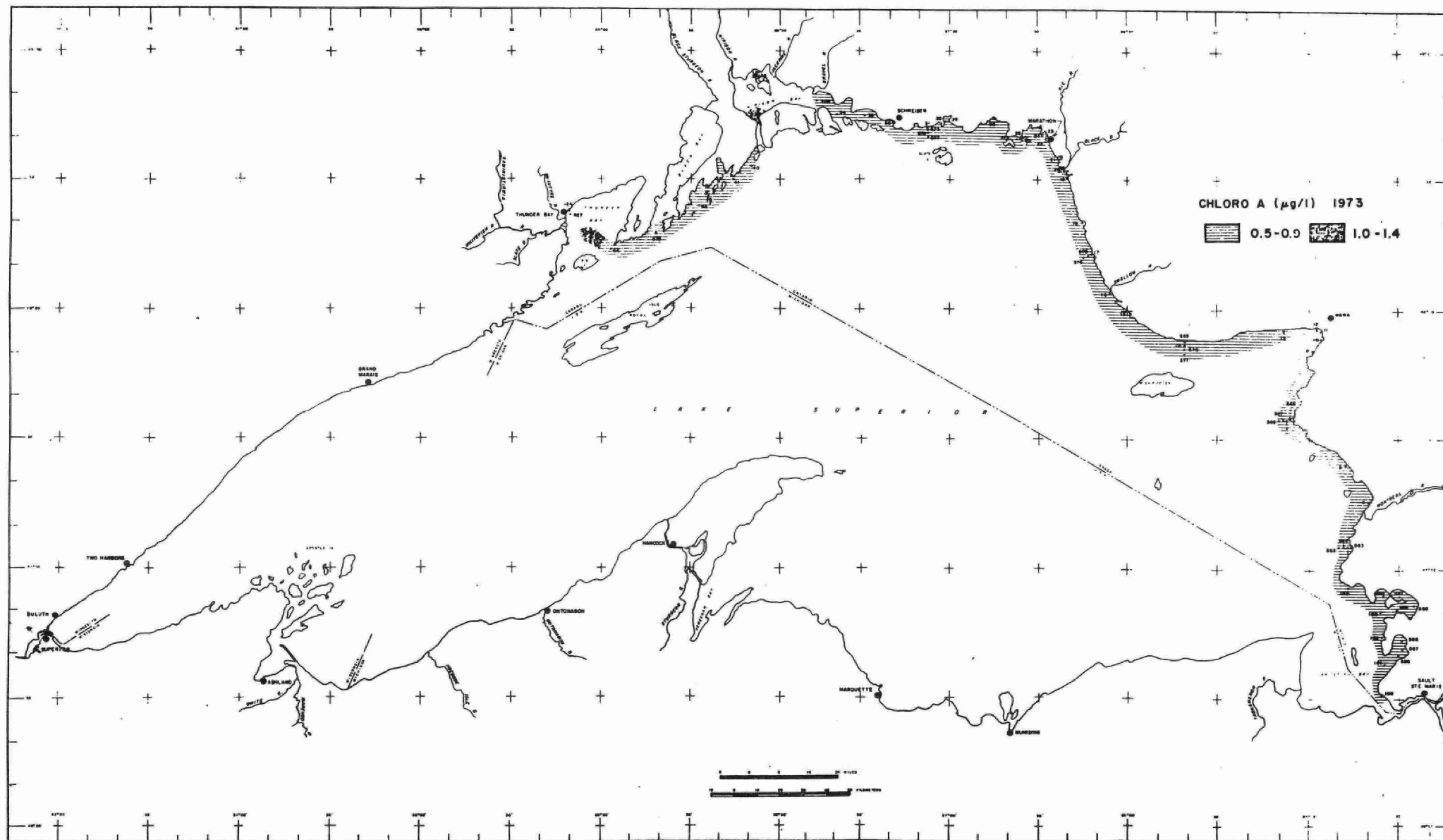
Figure 14 Mercury content of sediment core samples taken from Peninsula Harbour .

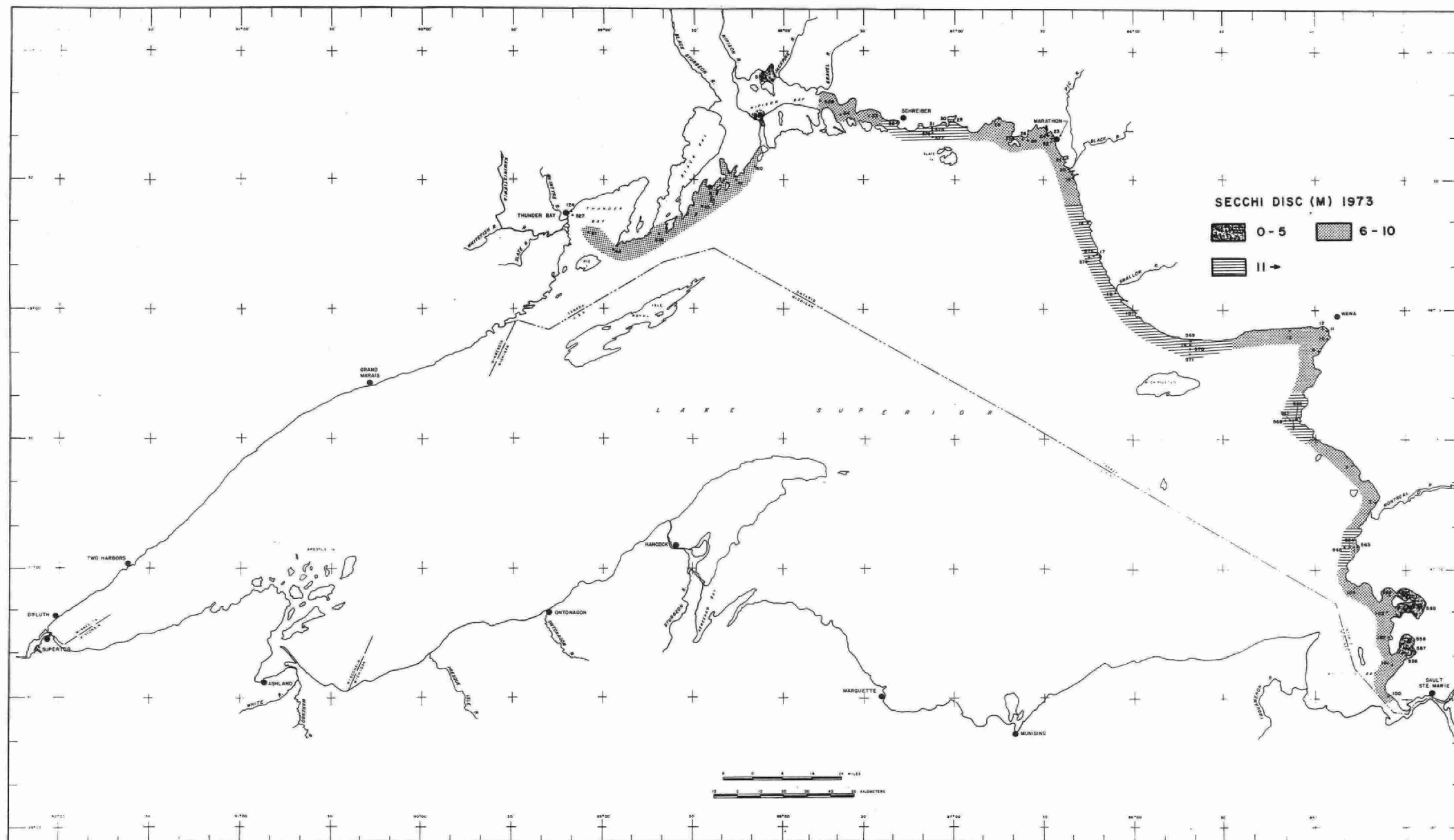




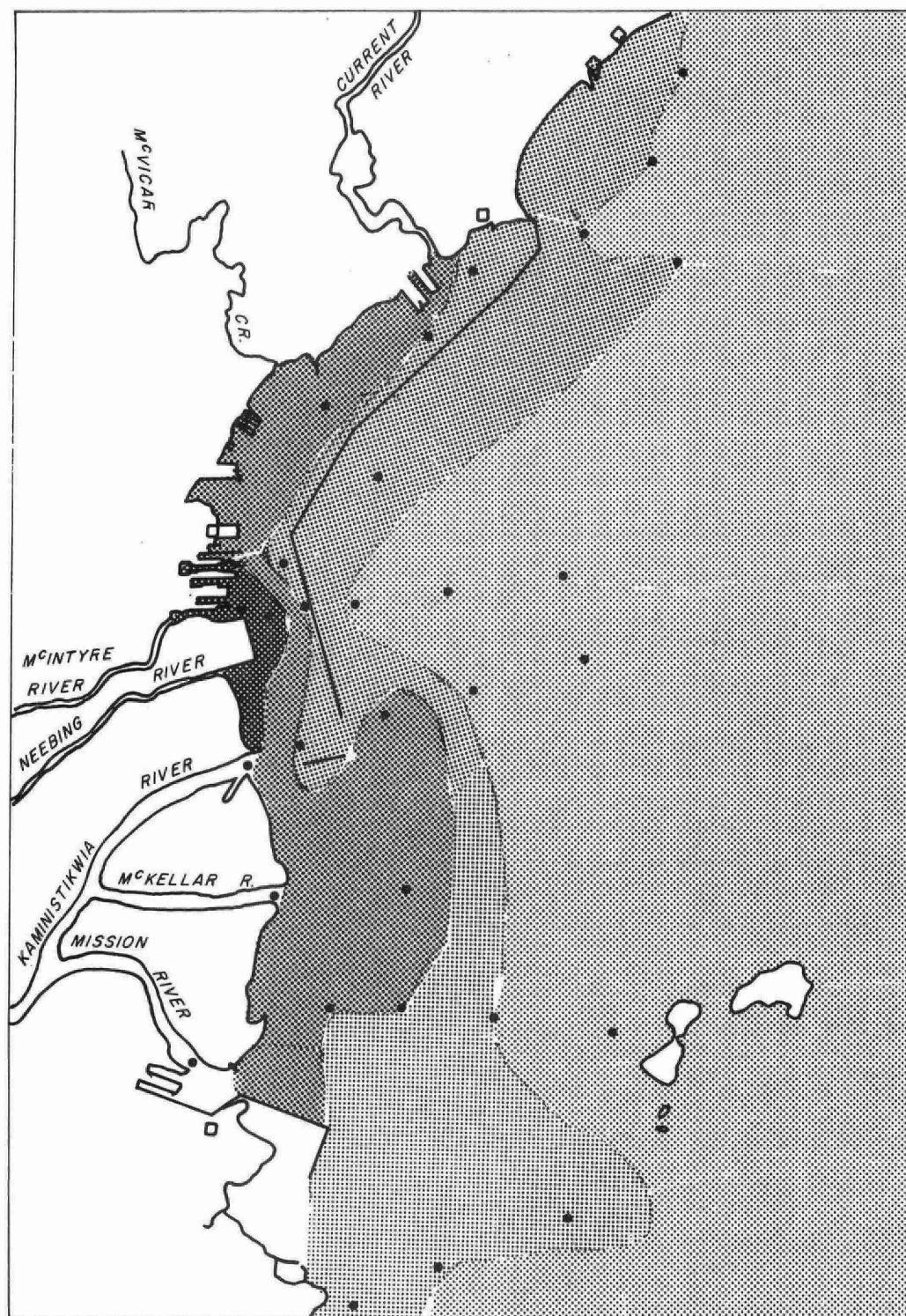








THUNDER BAY - 1973



CHLORO A ($\mu\text{g/l.}$)



0.5 - 0.9



1.5 - 1.8



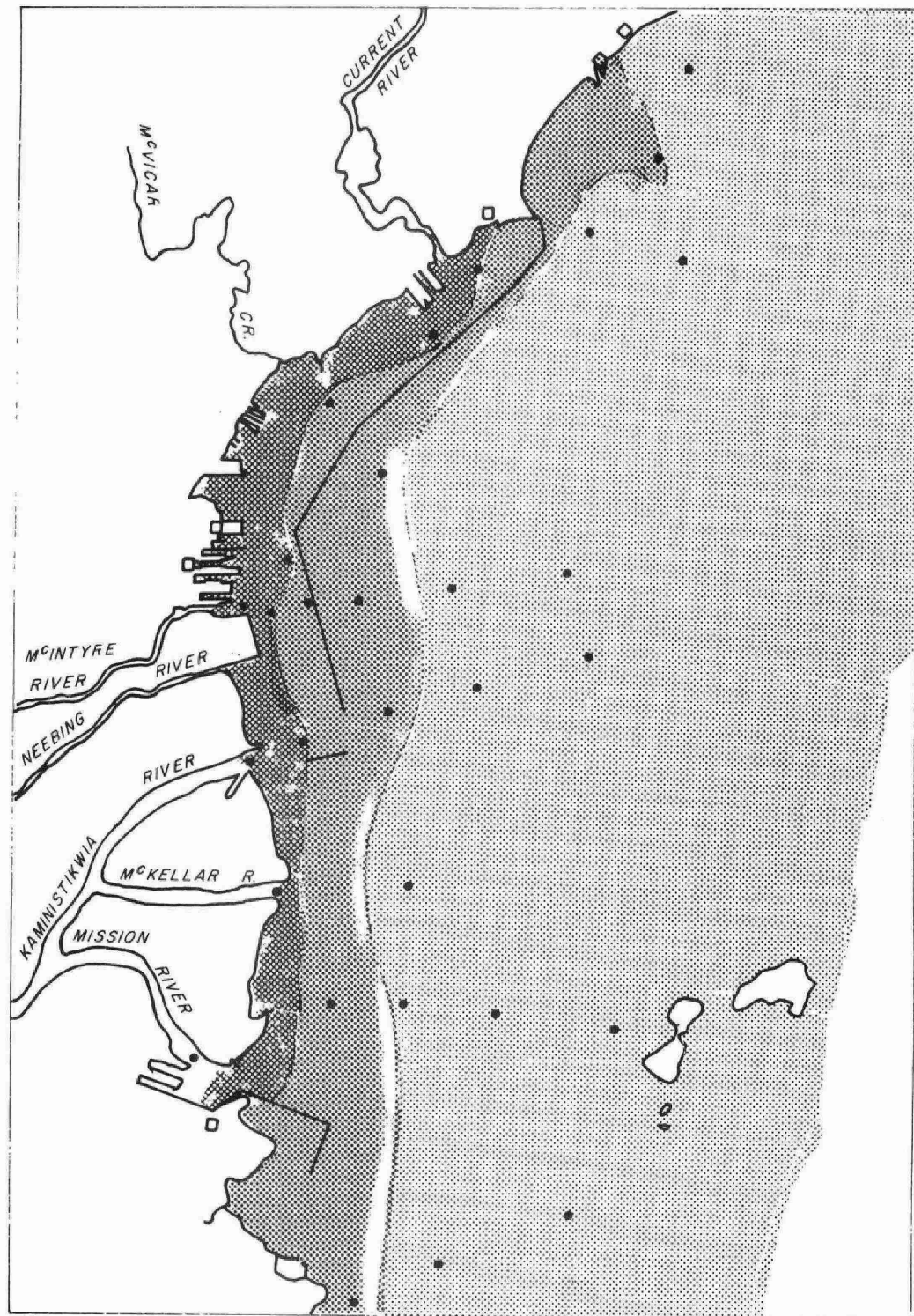
1.0 - 1.4



≥ 1.9

• - M.O.E. SAMPLING STATION

THUNDER BAY - 1973



TOTAL P ($\mu\text{g./l.}$)

≤ 10

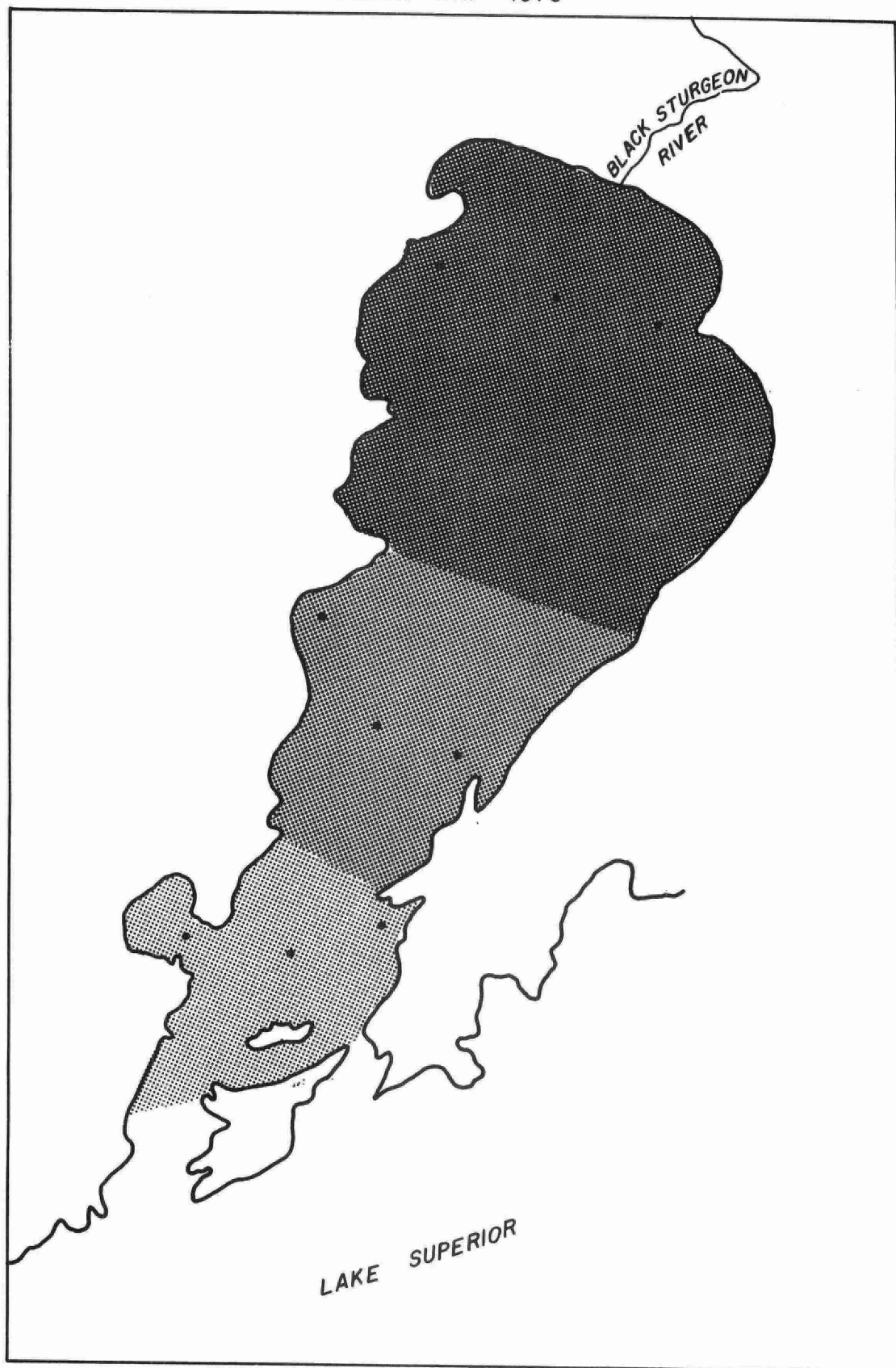
16-40

11-15

≥ 41

• - M.O.E. SAMPLING STATION

BLACK BAY — 1973



SECCHI DISK (M.)

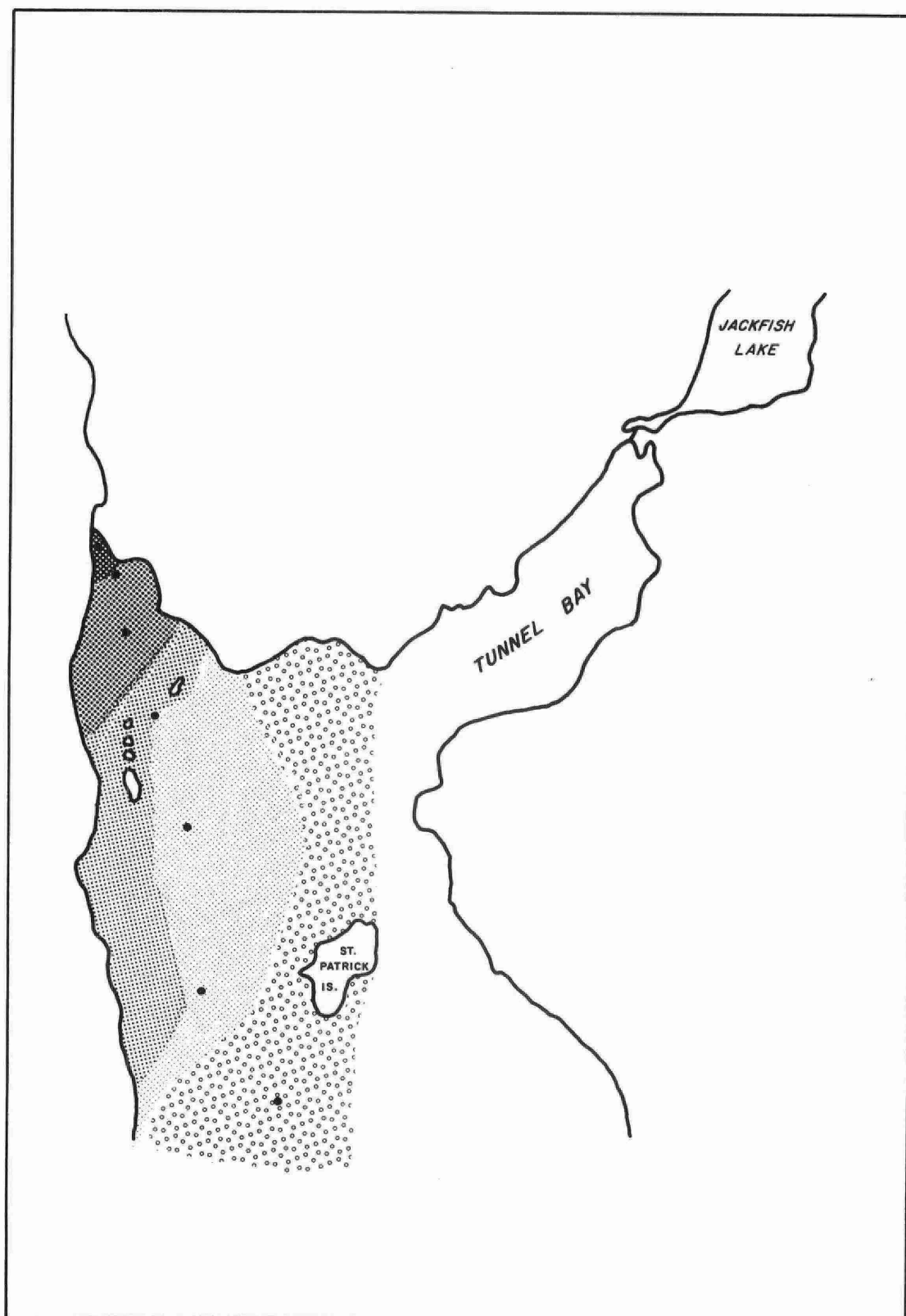
 ≥ 2.3

 1.9-2.2

 1.5-1.8

• — M.O.E. SAMPLING STATION

JACKFISH BAY — 1973



PHENOLS (mg/l)

1-5

6-10

11-14

15-60

≥ 61

• — M.O.E. SAMPLING STATION

CHROMIUM (mg/kg)

() ≤ 50.0

50.01 - 60.0

60.01-70.0

● >70.0

① 50.0

50.01 - 60.0

60.01-70.0

● >70.0

 $(\quad) \leq 50.0$

50.01-60.0

60.01-70.0

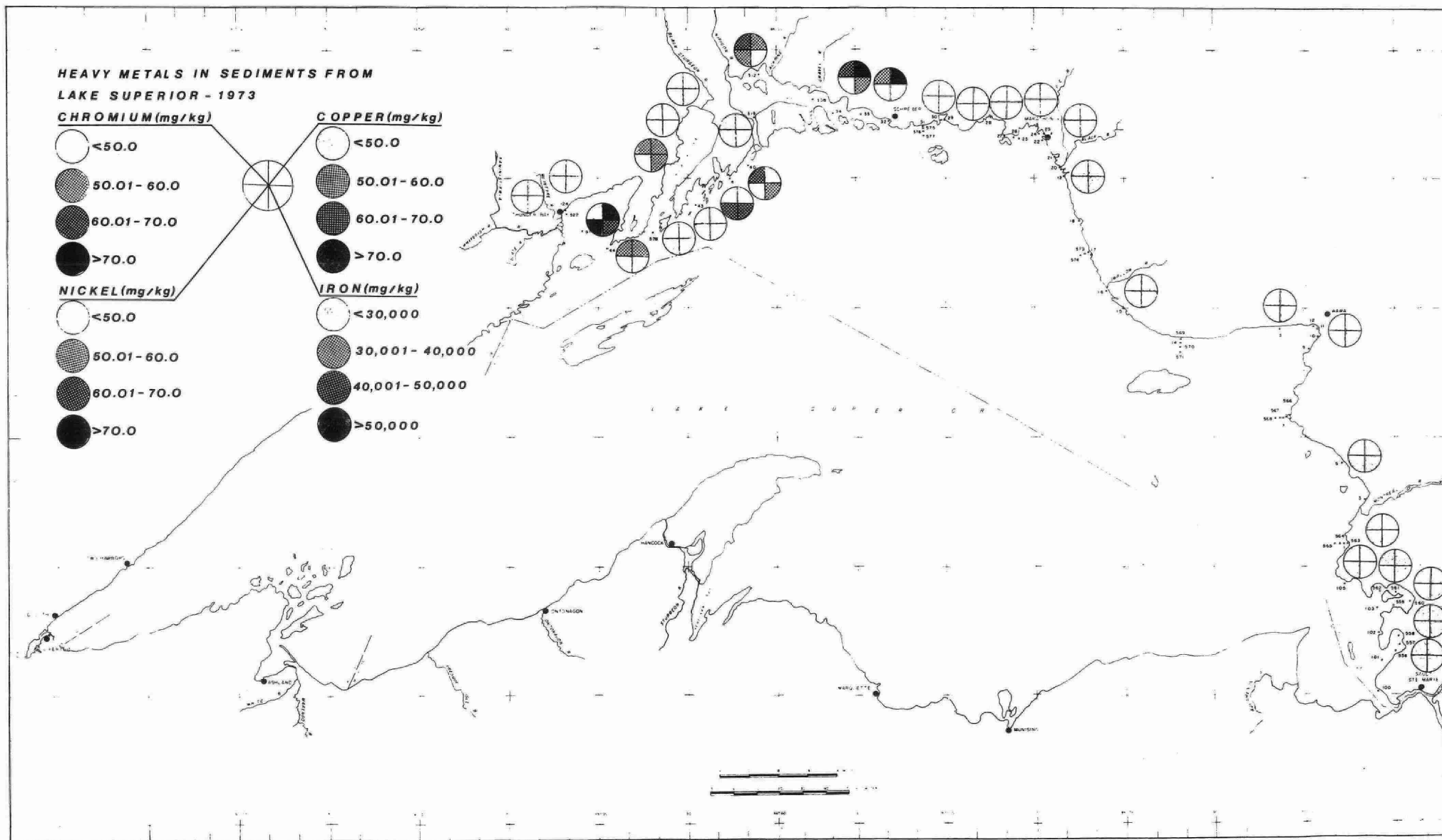
● >70.0

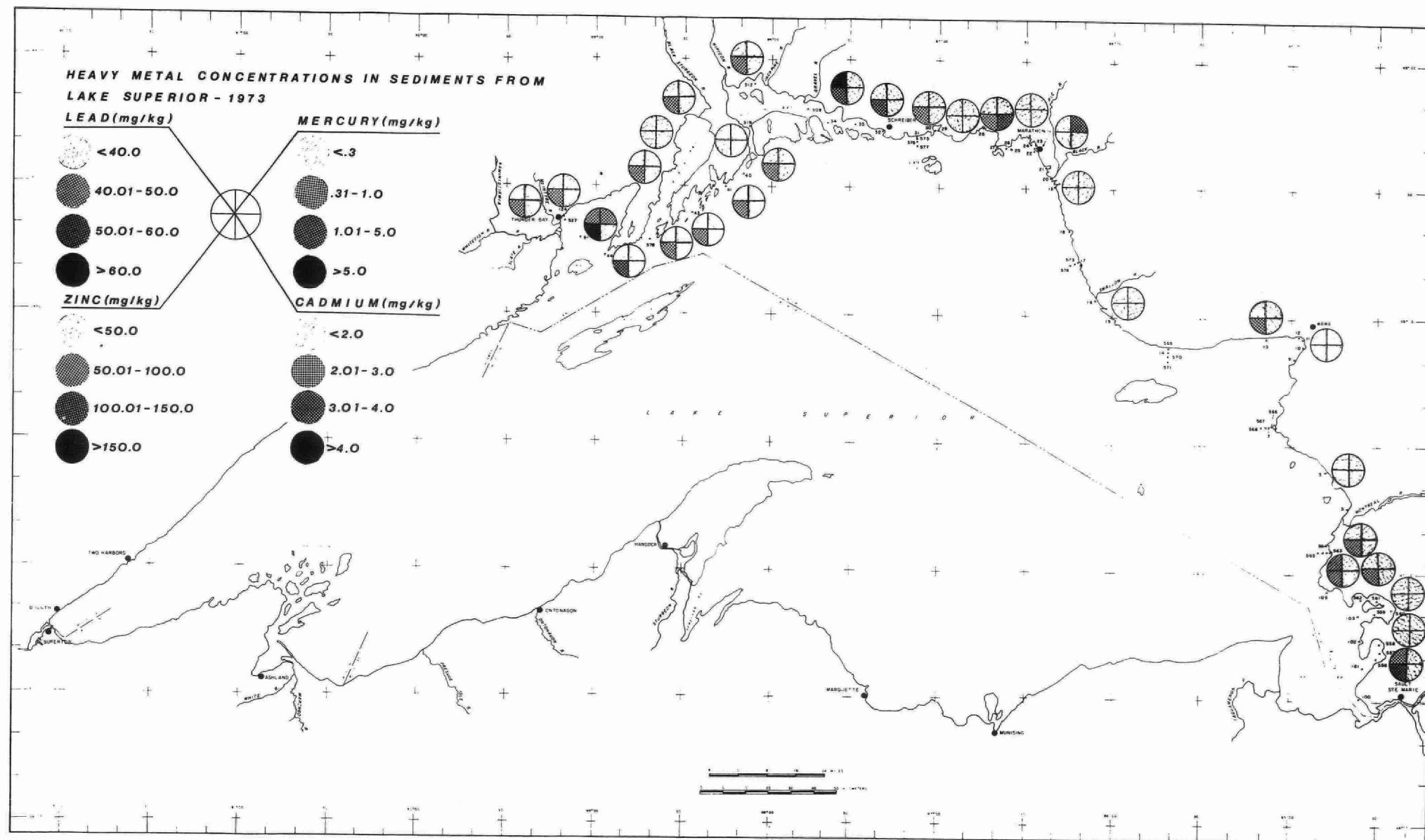
① $< 30,000$

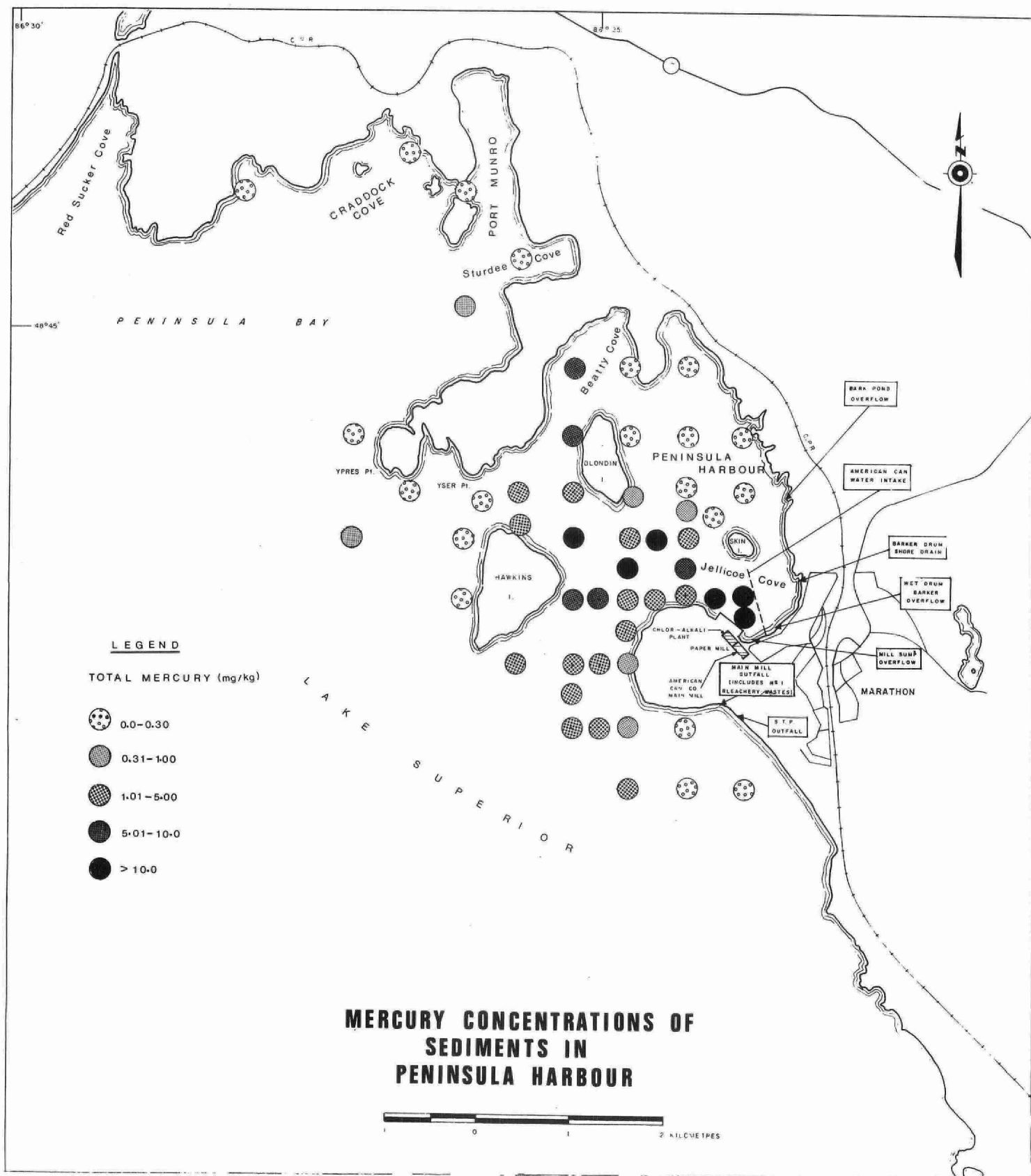
30,001 - 40,000

☒ 40,001-50,000

● >50,000







PENINSULA HARBOUR SEDIMENT SURVEY
MERCURY CONCENTRATIONS OF CORES

